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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The purpose of this project was to gain a fundamental understanding of the behavior of polymer molecules at surfaces and interphases so as to provide a basis for the design of these important properties. The first accomplishment completed was the development of a technique for the determination of interfacial tension of polymers by robust shape analysis of the profiles of molten polymer pendant drops. This technique was then applied to several materials systems: concentrated polymer solutions, miscible polymer blends, binary homopolymer immiscible blends, functionally terminated homopolymers, and		

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ternary blends of a block copolymer with its two immiscible parent homopolymers. The concentration dependence of surface tension of semidilute polymer solutions as measured and found to deviate from theoretical predictions, giving a power law dependence significantly weaker than that predicted for both good solvent, repulsive interface and theta solvent, repulsive interface conditions. In miscible binary blends, surface tension measurements as function of molecular weight and temperature indicated strong surface adsorption of the component of lower interfacial energy. For example, the surface composition was found to be 70% in this component when the bulk composition was only 5%. X-ray photoelectron spectroscopy (XPS) experiments confirmed this data and showed that the surface segregation was directly proportional to the surface energy difference of the two components, and that the surface composition profile was consistent with mean field predictions. The interfacial tension between immiscible homopolymers was found to decrease linearly with temperature and fall off with decrease in molecular weight. A mean field square gradient theory was developed which reproduced the temperature dependence but over estimated the molecular weight dependence. The surface tensions of functionally-terminated oligomers showed that for strongly polar end groups, the surface tension decreased with increase in molecular weight, opposite of the trend normally observed. XPS results suggested that this behavior was related to depletion of end groups from the surface. Block copolymers were found to decrease the interfacial tension between two homopolymers. A strong surfactant behavior was found to be qualitatively consistent with mean field theory. Specifically for rubber modified epoxies, a weak relationship between interfacial tension and rubber particle size was established. Finally, the mono - and multilayer properties of functionally terminated oligomers were studied using Langmuir Blodgett techniques. The layer thickness was found to be directly proportional to molecular weight and the materials deposited in Z-deposition.



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"Characterization of Polymeric Surfaces and Interfaces"
(Project 24165-MS)

A Final Report to the

Army Research Office

on grant DAAL03-86-K-0133
for the period July 1, 1986 to December 31, 1988

by

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Program Objective

The overall research goal of this project was to investigate the fundamental behavior of surfaces and interfaces in multiconstituent polymers, and to develop a theoretical understanding of this behavior in order to gain the capability for the design of polymer surface/interphase properties. To this end, the surface and interphase properties of a number of carefully designed model systems have been characterized by surface and interfacial tensiometry and by x-ray photoelectron spectroscopy. The initial thrust of our experiments was to examine pure component surface and interfacial tensions. This data was used to either validate or construct predictive thermodynamic theories of polymeric interphase properties. The second thrust was to then search for methods by which these interphase properties could be modified without substantially changing the bulk material. This was accomplished by varying end-group chemistry, by blending, and by the addition of block copolymer surfactants. The paragraphs that follow summarize the important findings.

Significant Research Results

The following abstracts describe significant results of our research.

1. Development of a Technique for Interfacial Tension Measurement

A novel technique is presented for the determination of interfacial tension by analysis of axisymmetric fluid drop profiles. The technique couples recent developments in digital image acquisition and processing with modern methods for robust shape comparison. The entire algorithm for drop profile acquisition and analysis is executable on a personal computer and includes a facility for rotationally resistant smoothing of the drop profile. The general performance of the robust shape comparison algorithm and improvement in accuracy resulting from smoothing is illustrated by

analysis of simulated pendant dop profiles. The overall performance of the image acquisition hardware and profile analysis software is assessed by evaluating the surface tension of glycerin. The resultant value of 62.6 ± 0.3 dyn/cm (at $24.2 \pm 0.2^\circ\text{C}$) agrees well with the literature data for glycerin.

2. Surface Properties of Miscible Blends

The surface structure and properties of miscible blends of polystyrene (PS) with poly(vinyl methyl ether) (PVME) have been studied as a function of the blend composition and constituent molecular weights. The lower surface tension of the PVME compared to that of PS results in preferential adsorption of PVME at the surface. The surface PVME enrichment is characterized by measurements of the surface tension as a function of the temperature, accomplished with an automated pendant drop apparatus, and by x-ray photoelectron spectroscopy (XPS). Angle-dependent XPS has been used to determine the surface concentration profiles of the blend constituents. The results of these measurements demonstrate that: 1) the PVME surface concentration is elevated substantially from that in the bulk; 2) the integrated surface concentration gradient determined from XPS measurements can be modeled as a $\coth^2(z/\xi+b)$ profile where ξ is the screening length and 3) the degree of surface enrichment depends strongly on the blend composition and molecular weight of the constituents, correlating well with the surface energy difference between PS and PVME.

3. Interfacial Tension of Immiscible Blends

Interfacial tensions between immiscible homopolymers are measured by using an automated pendant drop apparatus, which utilizes video digital image processing technique. A recently developed robust shape analysis algorithm is used to analyze the experimental drop profiles. The data show the effect of temperature and number average molecular (M_n) on the

interfacial tension for the immiscible blends polystyrene-poly(methyl methacrylate), polybutadiene-poly(dimethylsiloxane) and polystyrene-hydrogenated 1,2-polybutadiene. Interfacial tension decreases linearly with temperature and increases with molecular weight. The data are well represented by an $C_1 + C_2 M_n^{-Z}$ dependence on molecular weight but are not of sufficient precision to determine a precise value for the exponent. The interfacial tension data for the latter blend system are compared with thermodynamic theories of polymeric interfaces. A square gradient theory approach, in conjunction with the Flory-Huggins expression for the free energy of mixing, predicts a magnitude and temperature dependence of interfacial tension which are in reasonable agreement with experimental data. The predicted molecular weight dependence corresponds well with experimental data at high molecular weights but severely underestimates the interfacial tensions for low molecular weights.

4. Relationship Between Interfacial Tension and Particle Size in Rubber Toughened Epoxies

The interfacial tension between carbomethoxy-terminated butadiene-acrylonitrile copolymers and an epoxy resin as a function of temperature and copolymer composition is investigated. Using a digital image processing technique, the shape of a pendant drop of the epoxy in the copolymer is determined. Analysis of the drop shape is performed by profile discrimination and subsequent robust shape analysis. The data are used to examine the relationship between interfacial tension and particle size of the dispersed copolymer-rich phase in rubber-modified epoxy resins, that are immiscible in the uncured state.

5. Block Copolymer "Compatibilizers" for Polymer Blends

The compatibilizing effect of block copolymer addition on the interfacial tension between two immiscible homopolymers is studied as a function

of the concentration of the additive for the ternary system polystyrene/1,2 polybutadiene/poly(styrene-b-1,2 butadiene). A sharp decrease in interfacial tension is observed with addition of small amounts of copolymer, followed by levelling off as the copolymer concentration is increased above the apparent critical micelle concentration (CMC). For concentrations below this critical concentration the interfacial tension reduction is essentially linear in the copolymer content and compares well with the predictions of Noolandi and Hong.

6. End-Group Effects on Polymer Surface Properties

Surface tension measurements on functionally terminated oligomers of poly(dimethyl siloxane) have been performed as a function of end-group type, molecular weight, and temperature. The results demonstrate that there are strong effects, especially for polar end groups. The molecular weight dependence of the surface tension of these materials is opposite that found normally in that it decreases with increase in molecular weight. That is, as the chain becomes longer, the terminal group, with higher surface energy, is repelled from the surface and has more freedom to leave the surface thereby lowering the overall surface tension.

X-ray photoelectron spectroscopy (XPS) reveals that, for amine terminated oligomers, the surface is depleted in end-groups.

7. End-Group Effects on Interfacial Tension

The interfacial tensions between oligomers of polybutadiene and poly(dimethyl siloxane) (in the range of 1-3 dyn/cm) have been previously reported. It was discovered that the incorporation of amine end groups on the siloxane homopolymer decreased the interfacial tension by approximately 2 dyn/cm.

As would be expected, this modification also leads to a reduction in the apparent critical temperature of the blend measured by a cloud determination, and leads to apparent miscibility in certain cases.

8. Langmuir-Blogett Films of Functionally Terminated Oligomers

A computerized Langmuir trough has been designed and constructed for the formation and compression of monolayers of α,ω -functionally terminated poly(dimethyl siloxane) oligomers. The trough utilizes a precision micro-stepping motor to achieve very high resolution in the area vs. barrier location measurement. This resolution is critical in the constant surface pressure transfer of the monolayer to substrates.

Surface pressure-area isotherms reveal a number of transitions as monolayers of these materials are compressed. In particular, a transition preceding collapse is found to occur at an area that is independent of molecular weight. Analysis of transferred multilayers by XPS and surface plasmon spectroscopy provides evidence for the formation of hairpin-like configurations under these conditions, where the end-groups are attached to the substrate. These results also indicate that transfer occurs by z-deposition.

Radiation polymerizable monolayers are being synthesized by reacting hydroxyl terminated oligomers with maleic anhydride to form unsaturated acid end-groups on the oligomer.

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6. Technical Report #1; same as 1
7. Technical Report #2; same as 4
8. Technical Report #3; same as 3
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